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## Passivation of oxygen vacancy states in Hf O 2 by nitrogen

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# Passivation of oxygen vacancy states in $\text{HfO}_2$ by nitrogen

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Nitrogen is known to reduce leakage currents and charge trapping in high-dielectric-constant gate oxides such as  $\text{HfO}_2$ . We show that this occurs because nitrogen, substituting for oxygen atoms next to oxygen vacancy sites, repels the occupied gap states due to the neutral and positively charged oxygen vacancies out of the band gap into its conduction band. The state of the negatively charge vacancy is also repelled upwards but remains as a shallow gap state. This occurs because the vacancy becomes effectively positively charged; the adjacent Hf ions relax outwards from the vacancy and shift its states upwards. We show this using *ab initio* calculation methods which do not require an empirical correction to the band gap. © 2006 American Institute of Physics.

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## INTRODUCTION

The decrease of dimensions of complementary metal oxide silicon (CMOS) transistors has led to a need to replace the  $\text{SiO}_2$  gate oxide with an oxide of higher dielectric constant ( $K$ ) such as  $\text{HfO}_2$ , in order to maintain a small gate leakage current.<sup>1,2</sup> The oxide must satisfy various conditions such as be stable in contact with Si and have sufficient band offsets for both electrons and holes. However,  $\text{HfO}_2$ -based gate stacks show some inferior properties, including atomic diffusion, growth of interfacial  $\text{SiO}_2$  next to the Si, low temperature crystallization, increased boron penetration, and poorer trapping and electrical stability than those with  $\text{SiO}_2$ .

Incorporating nitrogen has been found to have some beneficial effects on the structural stability of high  $K$  oxide layers, particularly lower atomic diffusion rates (B, As, P, and O), reduced interfacial layer growth, raised crystallization temperatures, and lower boron penetration.<sup>3–9</sup> Nitrogen also has a beneficial effect on electrical properties, increasing the dielectric constant,<sup>8</sup> reducing the leakage currents, and improving the electrical stability.<sup>9–14</sup> The leakage current reduction occurs at lower fields, where the Poole-Frenkel hopping and trap-assisted tunnelling<sup>15</sup> are each found to be reduced. This points to a reduction in the density of gap states. Recently, experiment and theory<sup>16,17</sup> have shown that oxygen vacancies in  $\text{HfO}_2$  give rise to defect levels in the upper gap at 0.5–1.8 eV below its conduction band edge, consistent with recent defect band models,<sup>18</sup> so that O vacancies are a likely origin of this conduction pathway.

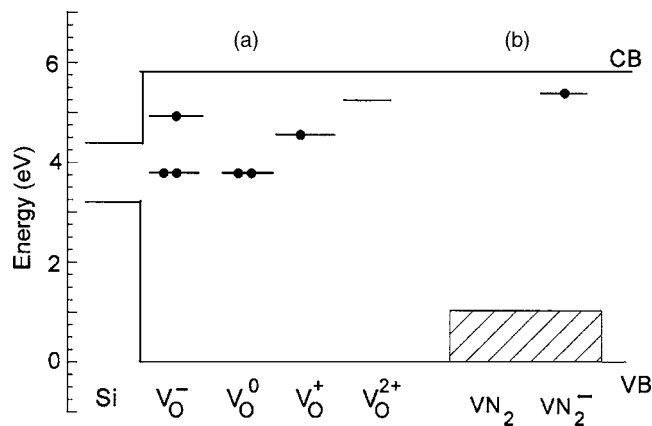
It is important to understand the origin of the beneficial effects of nitrogen on the electrical properties.<sup>19–21</sup> An interesting model of Umezawa *et al.*<sup>19</sup> noted that if two nitrogen atoms substitute for oxygens next to an O vacancy, this tends to push the vacancy level up out of the gap. However, they were unable to fully confirm this idea because their calculation method uses the local density approximation (LDA).

This is well known to underestimate the band gap and can misplace the localized defect energy levels. In this paper, we carry out calculations using *ab initio* local density-based methods which give accurate band gaps to show that the neutral vacancy level is indeed moved above the conduction band edge. We also consider the states of the negative vacancy not considered by Umezawa *et al.*<sup>19</sup> Finally we discuss the bonding rules which explain this behavior more generally.

## METHOD

The calculations are carried out on 48 atom primitive body-centered cubic supercells of cubic  $\text{HfO}_2$  containing the vacancy and the two nitrogen atoms. The total energy and electronic structure were calculated using the CASTEP plane-wave code.<sup>22</sup> For structural relaxation the total energies were minimized using ultrasoft pseudopotentials, a plane-wave cutoff energy of 340 eV and with the Perdew, Burke, Ernzerhof (PBE) exchange-correlation functional of the generalized gradient approximation (GGA). The band energies were then calculated for this structure using the screened exchange (sX) method. The sX method is based on Hartree-Fock, but describes electron correlation by a simple screening term.<sup>23–25</sup> It is a well-tested method that uses norm-conserving pseudopotentials and it has been found to give good band gaps for a range of semiconductors and oxides.<sup>24,25</sup> It was previously used to study oxygen vacancies and interstitials in  $\text{HfO}_2$ .<sup>17</sup> A plane-wave cutoff energy of 600 eV is used for sX due to the harder norm-conserving pseudopotentials. We also calculated energy levels with the weighted density approximation (WDA),<sup>26</sup> a less tested method. This also gives improved band gaps,<sup>27</sup> and can use ultrasoft pseudopotentials, allowing much lower plane-wave cutoff energies and faster calculations. The defects are modeled as single defects within periodic supercells. The supercells should contain at least 48 atoms because of the sizable lattice relaxations around each defect. We relaxed the structure in GGA and calculated energy levels and local density of states with sX or WDA.

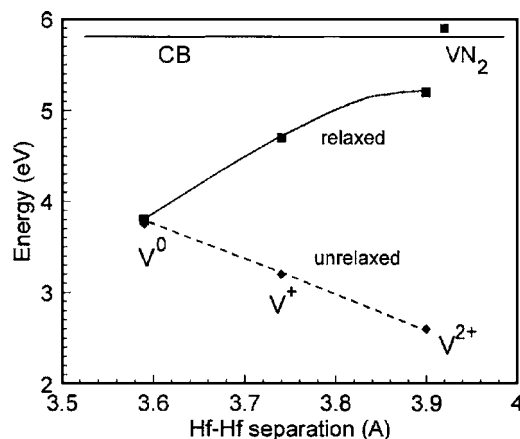
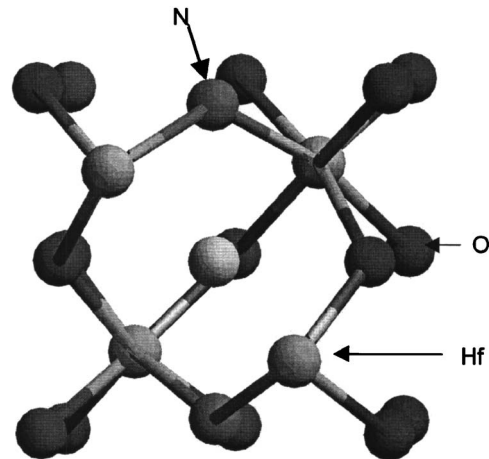
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FIG. 1. Energy levels of the (a) simple O vacancy and (b) the  $VN_2$  center.

Relaxation within sX or WDA was not possible due to limits on computer time.

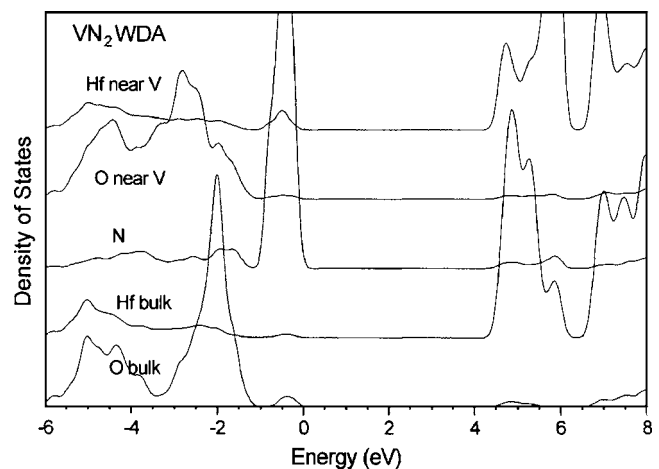
## RESULTS

The band gap of cubic  $HfO_2$  is 5.6 eV in sX, 6.1 eV in WDA, compared to 3.5 eV in GGA.<sup>28</sup> In pure  $HfO_2$ , the oxygen vacancy gives an energy level of  $A_1$  symmetry deep in the gap localized on its adjacent Hf ions. It is occupied by two electrons for the neutral vacancy,  $V^0$ . Emptying this level gives the  $V^+$  and  $V^{2+}$  charge states, Fig. 1(a). We relaxed the structure in GGA and calculated energy levels and local density of states with sX. We find that the energy levels of the unrelaxed vacancy fall in the gap, from 3.75 to 3.2 to 2.6 eV for the  $V^0$ ,  $V^+$ , and  $V^{2+}$  states. This ordering is due to the repulsion of electrons when there are two electrons in the defect state. On the other hand, if the atomic positions can relax, the energy levels rise with increasing charge, from 3.8 to 4.7 to 5.2 eV for  $V^0$ ,  $V^+$ , and  $V^{2+}$  states,<sup>17</sup> see Fig. 1(a). This is because the Hf ions adjacent to the vacancy relax outwards with increasing vacancy positive charge, which raises the levels. The Hf–Hf separation increases from 3.59 to 3.74 to 3.90 Å for  $V^{2+}$ ,  $V^0$ ,  $V^+$ , and  $V^{2+}$  states, from the bulk value of 3.54 Å. This is summarized in Fig. 2 which plots the energy levels for each charge state against the Hf separation. Thus the effect of relaxation dominates the effect of Coulombic repulsion, and the levels rise in the gap.

FIG. 2. Variation of the vacancy  $A_1$  energy level with Hf–Hf ion separation.FIG. 3. View of the relaxed  $VN_2$  center in  $HfO_2$ , Hf=brown, O=red, and N=blue. The vacancy is pale pink. Note the inward relaxations of the nitrogens towards the vacancy.

The O vacancy can also trap electrons, giving  $V^-$  and  $V^{2-}$  states. The  $V^0$  configuration has only the  $A_1$  gap state, with no other gap state above it. However, if an extra electron is placed on the vacancy, it undergoes an asymmetric relaxation which allows it to trap the electron in an extra state which is pulled out of the conduction band (CB). It is a singly degenerate state of  $B_1$  symmetry. This state lies about 0.8 eV below the CB edge in sX in pure  $HfO_2$  [Fig. 1(a)]. This is the fast electron trap seen in many trapping studies on  $HfO_2$ .<sup>11,18,30</sup>

We now substitute two nitrogen atoms for oxygens next to the vacancy, forming a neutral  $VN_2$  complex,  $VN_2^0$  (Fig. 3).<sup>17,29</sup> The atomic structure is relaxed in GGA, and the local density of states is calculated in GGA, sX, and WDA, for the adjacent Hf, O, and N ions to the vacancy, and on a bulk Hf ion. Figure 4 shows the density of states (DOS) in WDA. There is no gap state in either GGA, sX, or WDA, Figs. 1(b) and 4. The level previously formed by the vacancy has moved above the CB edge, due to a repulsion by the N's. The orbital character of the lower CB states is delocalized. The  $Hf^{4+}$  ions adjacent to the vacancy have relaxed away, so the separation is 3.90 and 3.94 Å, the same or greater than at the

FIG. 4. Calculated local density of states at the neutral  $VN_2$  center. Note the absence of gap states. Extra N-related states appear above the VB.

$V^{2+}$  in pure  $\text{HfO}_2$ . The nitrogen atoms have relaxed inwards towards the vacancy, compared to the equivalent oxygen sites.

The key point is that a nitrogen atom has one less valence electron than oxygen. Hence, when two nitrogens substitute for oxygens next to the neutral O vacancy, there would be a hole in the valence band of each N. The two electrons from the  $A_1$  level of  $V^0$  transfer to the N's to fill their valence states and form a closed shell. The  $A_1$  vacancy state is now empty for the neutral  $\text{VN}_2$  complex. Locally, the vacancy is  $V^{2+}$ . This charge causes an outward relaxation of Hf ions and increases the Hf–Hf separation to 3.90–3.94 Å as in the simple vacancy. This outward relaxation is actually slightly larger than at the  $V^{2+}$  center and it pushes the  $A_1$  state up in the gap. Indeed, it pushes it further than in pure  $\text{HfO}_2$ , so that the  $A_1$  state now lies above the CB edge. This is confirmed in the WDA calculation in Fig. 4, where the gap below the CB edge is clear for neutral  $\text{VN}_2$ . The same absence of gap states below the CB edge is found using sX. This confirms the result of Umezawa *et al.*,<sup>19</sup> using more robust methods. (Note that N introduces filled N 2*p* states above the oxide valence band edge, as shown by Shang *et al.*,<sup>21</sup> so the band gap of  $\text{HfO}_2\text{:N}$  is less than that of  $\text{HfO}_2$  itself, but there are no states below the CB.)

We found that the  $\text{VN}_2$  is still able to trap one electron. The electron can again induce an asymmetric distortion which pulls a  $B_1$  symmetry state down from the conduction band, Fig. 1(b). The DOS was calculated by sX and WDA. However, there is now no  $A_1$  state below it. The  $B_1$  state has a much smaller binding energy of 0.5 eV than in simple  $V_O$ . Thus it is a shallow trap.

Now consider the experimental situation. While the  $\text{HfO}_2$  gate oxide films are grown in an O-rich ambient, the gate electrode is subsequently deposited in the reducing conditions of metal-rich or silane chemistry. The relative ease of O diffusion in the  $\text{HfO}_2$  film means that oxygen vacancies tend to be the dominant defect in  $\text{HfO}_2$  films after processing the gate stack. The Fermi level would lie in the vacancy states in the oxide's upper gap.

Nitrogen can be introduced during growth or by post-deposition anneals in  $\text{N}_2$  or  $\text{NH}_3$ . The N is attracted towards the vacancy (0.44 eV binding energy<sup>19</sup>). The N inhibits further O diffusion. The  $\text{VN}_2$  center is overall neutral, so that it is no longer a charged center which could give rise to remote Coulombic scattering of carriers in the Si channel. It may give quadrupolar scattering, but this is much weaker. Reduction in the Si carrier mobility has been the another problem in devices with high *K* oxide dielectrics. Trap-assisted tunnelling and Poole-Frenkel hopping will be inhibited in  $\text{HfO}_2\text{:N}$  by the absence of gap states for  $\text{VN}_2^0$  to permit any resonant tunnelling. Even in disordered cases where the levels may possibly lie below the CB edge, the smaller trap depth would reduce trap-assisted tunnelling. Electron trapping is the source of transient threshold voltage instabilities in  $\text{HfO}_2$ -based field-effect transistors (FETs).<sup>18</sup> The much smaller trap depth of the electron level associated with  $\text{VN}_2^-$  in Fig. 1(b) means that any trapped electrons would soon be released back to the conduction states. This will reduce the degree of instability.

Charge transfer between  $V_O$  states and the gate electrode to create trapped holes was proposed by Shiraishi *et al.*<sup>31</sup> as a cause of the dc gate threshold voltage shifts seen in FETs due to the interaction between  $\text{HfO}_2$  dielectric and poly-Si gates.<sup>32</sup> In this model, N would have a large beneficial effect of removing the vacancy gap states which drive this mechanism. It would be a way to verify this mechanism, compared to that of Fermi level pinning by Hf–Si bonds.<sup>33</sup>

Other configurations of N in  $\text{HfO}_2$  are possible. Gavartin *et al.*<sup>20</sup> studied a wide range of other nitrogen configurations. However, those all produced deep gap states. It is also necessary to consider the combined effect of N and H, when  $\text{NH}_3$  is used. Hydrogen is also a source of fixed charge. Nevertheless, the simplicity of its formation and charge compensation at  $\text{VN}_2$  makes it an appealing model for the beneficial effect of N on trapping and leakage.

We finally consider the chemical bonding at the  $\text{VN}_2$  complex. If excess nitrogen is added to  $\text{HfO}_2$  containing O vacancies, the N is attracted towards the vacancy by a 0.44 eV binding energy.<sup>19</sup> But why does N not simply annihilate the vacancy to form a substitutional  $\text{N}_O$  site? The point is that the  $\text{VN}_2$  center is a closed shell species. In this, although the V is a structural vacancy, in terms of valence and closed shells it is not a “chemical” vacancy. It is similar to lattice vacancies in complex oxides such as a bixbyite ( $\text{In}_2\text{O}_3$ ) or a spinel ( $\gamma\text{-Al}_2\text{O}_3$ ). There is a partial occupancy of a sublattice which can be called vacancies, O site vacancies for  $\text{In}_2\text{O}_3$  and Al site vacancies for  $\text{Al}_2\text{O}_3$ , but these are required by valence. Despite the presence of lattice vacancies in these compounds, they do *not* give rise to gap states because they are closed shell systems. Thus in  $\text{HfO}_2\text{:N}$ , the neutral  $\text{VN}_2$  center is a stable closed shell system and the vacancy is required. In the oxynitrides, the absence of gap states below CB was also clearly seen in the density of states of the supercell compounds  $\text{Hf}_8\text{O}_{10}\text{N}_4$  and  $\text{Hf}_{10}\text{O}_8\text{N}_8$  studied by Shang *et al.*,<sup>21</sup> although the importance of this was not recognized then. These compounds contain two and four  $\text{VN}_2$  units per cell, respectively.

<sup>1</sup>G. Wilk, R. M. Wallace, and J. M. Anthony, J. Appl. Phys. **89**, 5243 (2001); J. Robertson, Eur. Phys. J.: Appl. Phys. **28**, 265 (2004).

<sup>2</sup>J. Robertson, J. Vac. Sci. Technol. B **18**, 1785 (2000).

<sup>3</sup>S. Jeon, C. J. Choi, T. Y. Seong, and H. Hwang, Appl. Phys. Lett. **79**, 245 (2001).

<sup>4</sup>M. R. Visokay, J. J. Chambers, A. L. P. Rotondaro, A. Shanware, and L. Colombo, Appl. Phys. Lett. **80**, 3183 (2002).

<sup>5</sup>Y. Morisaki, T. Aoyama, Y. Sugita, K. Irino, T. Sugii, and T. Nakamura, Tech. Dig. - Int. Electron Devices Meet. **2002**, 861.

<sup>6</sup>C. H. Choi, T. S. Jeon, R. Clark, and D. L. Kwong, IEEE Electron Device Lett. **24**, 215 (2003).

<sup>7</sup>M. A. Quevedo-Lopez *et al.*, J. Appl. Phys. **97**, 0435508 (2005).

<sup>8</sup>M. Koyama, Tech. Dig. - Int. Electron Devices Meet. **2002**, 849.

<sup>9</sup>H. J. Cho, C. S. Kang, K. Onishi, S. Gopalan, R. Nieh, R. Choi, S. Krishnan, and J. C. Lee, IEEE Electron Device Lett. **23**, 249 (2002).

<sup>10</sup>R. J. Carter, E. Cartier, A. Kerber, L. Pantisano, T. Schram, and S. DeGendt, Appl. Phys. Lett. **83**, 533 (2003).

<sup>11</sup>A. Shanware, Tech. Dig. - Int. Electron Devices Meet. **2003**, 939.

<sup>12</sup>C. S. Kang *et al.*, Appl. Phys. Lett. **81**, 2593 (2002).

<sup>13</sup>J. F. Kang *et al.*, IEEE Electron Device Lett. **26**, 237 (2005).

<sup>14</sup>X. G. Liu, F. Zhum, M. Yamada, and D. L. Kwong, IEEE Trans. Electron Devices **51**, 1798 (2004).

<sup>15</sup>M. Houssa, M. Touminen, M. Naili, V. Afanasev, A. Stesmans, S. Haukka, and M. M. Heyns, J. Appl. Phys. **87**, 8615 (2000).

<sup>16</sup>H. Takeuchi, D. Ha, and T. J. King, J. Vac. Sci. Technol. A **22**, 1337



- (2004).
- <sup>17</sup>K. Xiong, J. Robertson, M. C. Gibson, and S. J. Clark, Appl. Phys. Lett. **87**, 183505 (2005).
  - <sup>18</sup>A. Kerber *et al.*, IEEE Electron Device Lett. **24**, 87 (2003).
  - <sup>19</sup>N. Umezawa *et al.*, Appl. Phys. Lett. **86**, 143507 (2005).
  - <sup>20</sup>J. L. Gavartin, A. L. Shluger, A. S. Foster, and G. I. Bersuker, J. Appl. Phys. **97**, 053704 (2005).
  - <sup>21</sup>G. Shang, P. W. Peacock, and J. Robertson, Appl. Phys. Lett. **84**, 106 (2004).
  - <sup>22</sup>V. Milman, B. Winkler, J. A. White, C. J. Pickard, and M. C. Payne, Int. J. Quantum Chem. **77**, 895 (2000).
  - <sup>23</sup>B. M. Bylander and L. Kleinman, Phys. Rev. B **41**, 7868 (1990).
  - <sup>24</sup>C. B. Geller, W. Wolf, S. Picozzi, A. Continenza, R. Asahi, W. Mannstadt, A. J. Freeman, and E. Wimmer, Appl. Phys. Lett. **79**, 368 (2001).
  - <sup>25</sup>R. Asahi *et al.*, Thin Solid Films **411**, 101 (2002).
  - <sup>26</sup>P. P. Rushton, D. J. Tozer, and S. J. Clark, Phys. Rev. B **65**, 235203 (2002).
  - <sup>27</sup>J. Robertson, K. Xiong, and S. J. Clark, Thin Solid Films **496**, 1 (2005).
  - <sup>28</sup>P. W. Peacock and J. Robertson, J. Appl. Phys. **92**, 4712 (2002).
  - <sup>29</sup>Y. P. Feng, A. T. L. Lim, and M. F. Li, Appl. Phys. Lett. **87**, 062105 (2005).
  - <sup>30</sup>S. Zafar, A. Kumar, E. Gusev, and E. Cartier, IEEE Trans. Device Mater. Reliab. **5**, 45 (2005).
  - <sup>31</sup>K. Shiraishi *et al.*, Jpn. J. Appl. Phys., Part 2 **43**, 1413 (2004).
  - <sup>32</sup>C. Hobbs *et al.*, IEEE Trans. Electron Devices **51**, 971 (2004); **51**, 978 (2004).
  - <sup>33</sup>K. Xiong, P. W. Peacock, and J. Robertson, Appl. Phys. Lett. **86**, 012904 (2005).